Periodicity of Elements

Mendeleev classified the elements on the basis of their atomic weights. Henry Moseley in 1911 proposed the modern periodic law as: *the physical and chemical properties of the elements are the periodic functions of their atomic number.* The modern periodic table recommended by IUPAC (The International Union of Pure and Applied Chemistry) is based on the electronic configurations of elements.

There are **18** vertical columns or **groups** and **7** horizontal **periods** in the modern periodic table. The modern periodic table is also called the long form of the periodic table.

On the basis of the filling order of orbitals the periodic table can be divided into four regions or blocks representing the filling of particular subshells.

(i) *s*-block Elements:

The elements in which the differentiating electron (or the last electron) enters into the nth shell are called the *s*-block elements. The first two groups on the left side of the periodic table (1 and 2 groups) comprise the *s*-block because they result from the filling of an *s*-orbital of the nth shell. They are characterized by an electronic configuration of ns^1 or ns^2 over a core with noble gas configuration [except H ($1s^1$) and He ($1s^2$)]. With the exception of H and He the groups 1 and 2 elements are called the alkali and alkaline earth metals, respectively.

(ii) *p*-block Elements:

The elements in which the differentiating electron enters into the *p*-orbitals of the nth shell are called the *p*-block elements. The six groups on the right side of the periodic table (columns 13 to 18 groups) comprise the *p*-block because they result from the successive filling of one of the *p*-orbitals of the nth shell. The elements have the general valence shell electronic configuration of the $ns^2np^{1\text{-}6}$. The elements of the groups 13, 14, 15, 16, 17, 18 have the valence shell electronic configuration of ns^2np^1, ns^2np^2, ns^2np^3, ns^2np^4, ns^2np^5 and ns^2np^6, respectively. The elements belonging to groups 15 (ns^2np^5),16 (ns^2np^4), 17 (ns^2np^5) and 18 (ns^2np^6) are called pnicogens, chalcogens, halogens and noble gases, respectively.

The elements belonging to groups 1 to 2 and 13 to 17 collectively are called the main group elements or representative elements.

(iii) *d*-block Elements or Transition Elements:

The ten groups in the middle of the periodic table (groups 3 to 12) comprise the *d*-block elements. In these elements the differentiating electron enters into one of the *d*-orbitals of the $(n-1)^{th}$ shell.

The transition elements are the elements of column 3 to 11 which have incompletely $(n-1)d$ subshell or readily produce cations with incompletely filled $(n-1)d$ subshell. The general valence shell electronic configuration of transition elements is $(n-1)\ d^{1-10}ns^{0-2}$ but there is no regular trend in electronic configuration, neither in a period nor in a group.

There are four transition series among the transition elements corresponding to the filling of 3d, 4d, 5d, and 6d orbitals of $(n-1)$ shell or the penultimate shell.

(a) 3d-Series or First Transition Series: This series has 10 elements: $_{21}$Sc to $_{30}$Zn. In these elements the differentiating electron enters into one of the 3*d* orbitals.

(b) 4d-Series or Second Transition Series: This series also has 10 elements: $_{39}$Y to $_{48}$Cd. In these elements the differentiating electron enters into one of the 4*d* orbitals.

(c) 5d-Series or Third Transition Series: This series also has 10 elements: $_{59}$La, $_{72}$Hf to $_{80}$Hg. In these elements the last electron enters into one of the 5d orbitals.

(d) 6d-Series or Fourth Transition Series: This series is incomplete. The first element of this series is $_{89}$Ac. The last electron enters into one of the 6d orbital.

(iv) *f*-block Elements or Inner Transition Elements:

The elements in which the differentiating electron enters into one of the *f*-orbitals of the $(n-2)^{th}$ shell or anti-penultimate shell are called *f*-block elements. These elements are shown at the bottom of the periodic table. There are two series of *f*-block elements called as lanthanides and actinides. In lanthanides electrons are filled progressively in the 4*f* subshell and in actinides electrons are filled progressively in the 5*f* subshell. Since these elements lie in between the transition elements, these elements are also called the inner-transition elements. The general valence shell electronic configuration of *f*-block elements is $(n-2)\ f^{0-14}(n-1)\ d^{\,0-2}\ ns^2$.

Notice that number of groups in a block correspond to the maximum number of electrons that can occupy the particular subshell of that block. The *s* block has two groups (corresponding to one *s* orbital accommodating a maximum of two electrons), the *p*-block has 6 groups (because a *p*-subshell accommodate a maximum of six electrons), the *d*-block has 10 groups (because a *d* subshell accommodates a maximum of 10 electrons) and the *f*-block has 14 groupss (because an *f* subshell accommodates a maximum of 14 electrons).

Discussion of periodic properties

(a) Effective Nuclear Charge (Z_{eff}): In a multielectron atom, nuclear charge experienced by a particular electron is reduced due to the repulsion with other electrons, including those in the same shell. In other words, electrons shield that particular electron from the influence of the nucleus. The reduction of the true nuclear charge (***Z***) to the effective nuclear charge (Z_{eff}) by the other electrons is called **shielding**. The net positive charge experienced by an electron due to the nucleus in a multi-electron atom is called effective nuclear charge (Z_{eff}). Effective nuclear charge (Z_{eff}) is expressed as

$$Z_{eff} = Z - \sigma$$

where σ is an empirical shielding constant estimated as sum of the shielding contributions from all other electrons.

Slater's rules: Slater proposed (1930) a set of empirical rules for estimating the shielding contributions by electrons in different orbitals. These are known as Slater's rules.

The rules:

(i) The electrons of the atom are divided into groups like:

(1s), (2s 2p), (3s 3p), (3d), (4s 4p), (4d), (4f), (5s 5p), (5d), ... etc.

The fraction (of e) contributed to shielding on any electron in a particular electron group by other electrons is now estimated as -

(ii) Electrons in groups on the right of the particular electron under consideration: **zero**.

(iii) Each other electron in the same group:

0.30 if the group is 1s; otherwise, **0.35**

(iv) If the electron under consideration belongs to an **(ns, np)** group:

- All electrons with a principal quantum number less by one: **0.85 each**.
- All electrons in groups further left: **1.0 each**.

(v) If the electron under consideration belongs to a ***d* or *f*** group:

- All electrons in groups lying left of this group: **1.0 each**.

How to apply Slater's rules? The following example shows how σ is estimated for the electrons in Iron Atom (Fe, Z = 26)

Ground state configuration:

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Electron groups: $(1s)^2$ $(2s2p)^8$ $(3s3p)^8$ $(3d)^6$ $(4s)^2$

(i) 1s Electron

- Shielding contributions:
  - Electrons in higher groups (right of 1s): **0**
  - Remaining electron in 1s: **0.30**
- Total shielding (σ):

  $\sigma = 0.30$
- Effective nuclear charge (Z_{eff}):

  $Z_{eff} = 26 - 0.30 = 25.70$

(ii) 2s or 2p Electron

- Shielding contributions:
  - Electrons in higher groups (right of 2s2p): **0**
  - 7 other electrons in same (2s2p) group: $7\times0.35=2.45$
  - 2 electrons in (n-1) group (1s): $2\times0.85 =1.70$
- Total shielding (σ):

  $\sigma=2.45+1.70=4.15$
- Effective nuclear charge (Z_{eff}):

  $Z_{eff}=26-4.15=21.85$

(iii) 3s or 3p Electron

- Shielding contributions:
  - Electrons in higher groups (3d, 4s): **0**
  - 7 other electrons in same (3s3p) group: $7\times0.35=2.45$
  - 8 electrons in (n-1) group (2s2p): $8\times0.85=6.80$
  - 2 electrons in groups further left (1s): $2\times1.0=2.00$
- Total shielding (σ):

  $\sigma=2.45+6.80+2.00=11.25$
- Effective nuclear charge (Z_{eff}):

  $Z_{eff}=26-11.25=14.75$

(iv) 3d Electron

- Shielding contributions:
  - Electrons in higher groups (4s): **0**
  - 5 other electrons in same (3*d*) group: $5\times0.35=1.75$

    - 18 electrons in all groups to the left of 3*d*: 18×1.0=18.0
- Total shielding (*σ*):

  σ=1.75+18.0=19.75
- Effective nuclear charge (Z_{eff}):

  Z_{eff}=26−19.75=6.25

(v) 4s Electron

- Shielding contributions:
    - 1 other electron in same (4s) group: 0.35
    - 14 electrons in (*n*−1) groups (3s3p and 3d): 14×0.85=11.9
    - 10 electrons in groups further left (≤(*n*−2): 10×1.0=10.0
- Total shielding (*σ*):

  σ=0.35+11.90+10.0=22.25
- Effective nuclear charge (Z_{eff}):

  Z_{eff}=26−22.25=3.75

Problem: Estimate σ and effective nuclear charge for a valence electron in the ground state of the nitrogen atom.

Problem: Estimate σ and effective nuclear charge for a valence 4*s* electron in the ground state of the zinc atom.

Problem: Estimate σ and effective nuclear charge for a 3*d* electron in the ground state of the zinc.

(b) Atomic Radius:

The size of an isolated atom is difficult to define and difficult to measure because:

(i) it is not possible to locate the exact position of electrons in an atom as an orbital has no sharp boundary.

(ii) of the wave nature of the electrons, the electron density does not stop at a certain distance from the nucleus but instead extends far away beyond the nucleus.

(iii) it is difficult to isolate an individual atom for its size determination (except noble gases).

(iv) the probability of finding the electrons round the nucleus in an atom is influenced by the presence of the neighbouring atoms, therefore, the size of the atom changes with the change of neighbouring atoms.

The size of an atom is usually defined in terms of its atomic radius. The atomic radius of an element is defined as half of the distance between the nuclei of neighbouring atoms in the pure element. Atomic radius can be defined in the following three ways:

(i) **Covalent radius**
(ii) Metallic radius
(iii) van der Waals' radius

(i) Covalent Radius

Covalent radius of an atom is half of the distance between the nuclei of two identical atoms (non-metals) when they are covalently bonded together. For example, in the Cl_2 molecule the distance between the two chlorine nuclei is 198 pm, therefore, the covalent radius of a chlorine atom is 198/2(= 99 pm).

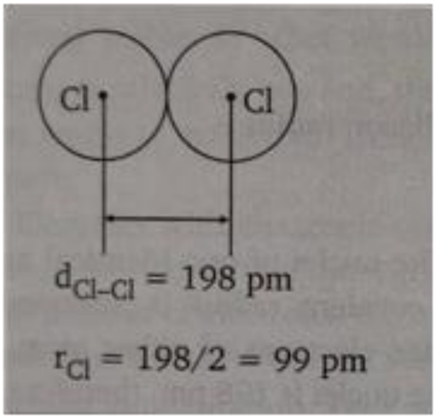


Figure: Covalent radius

The internuclear distance between two identical atoms A in a covalent bond is given by:

$$d_{A-A} = r_A + r_A = 2r_A$$

or

$$r_A = \frac{d_{A-A}}{2}$$

In the case of a heteronuclear polyatomic molecule AB, the internuclear distance d_{A-B} is equal to the sum of the covalent radii of atoms A (r_A) and B (r_B) bonded together by a covalent bond:

$$d_{A-B} = r_A + r_B$$

This equation holds true when:

- The bond between A and B is a single bond.
- The electronegativities of A and B do not differ significantly.

Experimental d_{A-B} values may differ from the sum of r_A+r_B due to:

(a) *Electronegativity Difference*

If A and B have a large electronegativity difference, the bond attains ionic character, consequently, the observed d_{A-B} is shorter than r_A+r_B. This ionic character arises from the electronegativity difference between atoms A and B. If B is more electronegative than A, the bonding electron pair shifts toward B, creating a partial negative charge on B and a partial positive charge on A. Resulting electrostatic attraction brings the atoms closer, reducing d_{A-B}. To account for this ionic character, the corrected bond length can be expressed by the Schomaker and Stevenson's Formula (1941):

$$d_{A-B} = r_A + r_B - 9(\chi_B - \chi_A)$$

where:

r_A and r_B are covalent radii of A and B (in pm),

χ_A and χ_B are electronegativities of A and B.

This expression is only valid for single bonds (no π bonds). Porterfield's refined the formula for better accuracy (including cases with π bonds) as:

$$d_{A-B} = r_A + r_B - 7(\chi_B - \chi_A)$$

(b) *Bond Multiplicity*

When two atoms are joined by multiple bonds, the bond length is shorter than the sum of their covalent radii. So, covalent radii are classified with respect to bond order as single bond radius, double bond radius and triple bond radius.

(c) *Steric Hindrance*

In molecules with bulky substituents (e.g., CCl_4, CBr_4), steric repulsion between groups lengthens bonds with the central atom.

(ii) Metallic Radius

For a metallic element, the metallic radius is defined as one half of the distance between two of the nuclei next to each other in a close pack crystal of the metal wherein metal exhibits a coordination number of 12. For example, the internuclear distance between two adjacent sodium atoms in a crystal of sodium metal is 380 pm. The metallic radius of Na metal is 380/2=190 pm. The metallic radius of an atom is slightly bigger than its single bond covalent radius.

(iii) van der Waals' Radius

It is defined as one half of the distance between the nuclei of two closest but non-bonded atoms of the same element.

When a molecular gas such as Cl_2, Br_2 and I_2 or a noble gas is frozen into a solid, the atoms of molecules or atoms of the noble gas are touching each other but are not bonded together by chemical bonds, instead are bonded together by weak forces, called the van der Waals' forces. In solid argon, for example, each molecule of the monatomic gas is 382 pm from 12 other molecules, therefore, van der Waals' radius of argon is 191 pm.

The value of the van der Waals' radius depends on the effective packing of molecules and is not a fixed quantity. Since, van der Waals' forces (or intermolecular forces) are weaker than intramolecular forces (i.e., covalent bonds), the internuclear distance between the nuclei of two non-bonded adjacent atoms of two adjacent molecules in liquid or solid molecular substance is greater than the distance between atoms covalently bonded to one another in a molecule. Thus, the value of van der Waals' radius of an atom is always greater than the value of covalent radius of that atom.

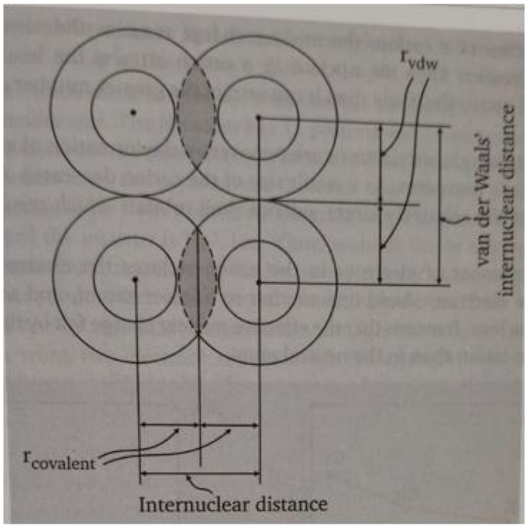


Figure: van der Waals radius and covalent radius

Periodic Trends in Atomic radii (*for ionic radii trends are same***)**

(i) In a Period: For the main group elements (the s- and p-block elements), the atomic radii decrease when moving left to right across a period of the periodic table.

Explanation: The trend in atomic radius from left to right across a period in the periodic table is determined by the strength of the force of attraction between the nucleus and the outermost electrons. The larger the effective nuclear charge, the stronger the hold of the nucleus on the outermost electrons, and the smaller the atomic radius. As we move left to right from one element to the next in a period, the number of electrons in the inner shell (i.e., the core electrons) remains constant, whereas the nuclear charge increases, and the electrons are added to the orbitals of the same outermost shell. The differentiating electrons that are added to the orbital of the same outermost shell are ineffective in shielding one another. Consequently, the effective nuclear charge increases steadily while the principal quantum number of the outermost shell remains constant. The increased effective nuclear charge attracts the outermost electrons more strongly, pulling them closer to the nucleus. Thus, the atomic radii of elements decrease when moving left to right in a period.

(ii) In a group: In general atoms of main group elements become larger in going from top to bottom within a group. This trend is well established for *s* and *p*-block elements.

Explanation: On going from top to bottom within a group, the number of shells as well as the nuclear charge increase. The increase in the number of shells tends to decrease the force of attraction between the nucleus and the valence electrons. This decreased force of attraction tends to increase the atomic radii. The increased nuclear charge tends to increase the force of attraction between the nucleus and the valence electrons. Thus, the increase in the number of shells tends to increase the atomic radii, whereas the increase in nuclear charge tends to decrease the atomic radii. The effect of the increase in the number of shells is usually more significant than that of the increased nuclear charge. As a result, the net force of attraction (i.e., effective nuclear charge, Z_{eff}) experienced by the valence electrons decreases on descending the group, and the atomic radii increase.

This variation can be explained by considering, for example, the size of atoms of alkali metals. Increase in atomic radius from K to Rb is much less compared to corresponding increase observed in moving from Na to K. This is due to the poor shielding effect of the 3d electrons.

Elements of Group I	Metallic Radii (in pm)
Li	123
Na	154
K	203
Rb	216
Cs	235

For Group 13 elements, on going from top to bottom within the group, the atomic radius is expected to increase primarily due to the addition of a new outermost shell with each succeeding element. However, there are some interruptions as we move from Al to Ga and In to Tl. The electronic configurations of Al and Ga are $[\mathrm{Ne}]3s^2 3p^1$ and $[\mathrm{Ar}]3d^{10}4s^2 4p^1$, respectively. The electrons present in the 3*d*-orbitals do not shield the outermost electrons effectively from the nucleus. Thus, the effective nuclear charge in Ga becomes somewhat greater than that in Al. Consequently, the atomic radius of Ga (135 pm) is slightly less than that of Al (143 pm). The size of a fifth-period element (In) is significantly larger than Ga because the shielding effect does not decrease significantly in going from Ga to In, but the number of shells increases. As expected, the size increases on going from In to Tl, but it is smaller than expected. The electronic configurations of In and Tl are $[Kr]\ 4d^{10}5s^2 5p^1$ and $[Xe]4f^{14}5d^{10}6s^2 6p^1$ respectively. Since the 4*f* orbitals present in Tl are larger in size than the *d* orbitals, the electrons in the 4*f* orbitals have a much poorer shielding effect. Thus, the effective nuclear charge for outermost electrons does not decrease significantly when going from In to Tl. Hence, the atomic radius of Tl (170 pm) is only slightly greater than that of In (167 pm).

In general, for the p-block elements, the atomic size generally increases down a group because the number of electron shells increases as we move from one period to the next. However, the increase is not uniform due to differences in shielding by d- and f-electrons.

- The atomic radius of the third-period element is significantly larger than that of the second-period element. This is because an additional electron shell is added, increasing the distance of the valence electrons from the nucleus.
- The increase in atomic size from the third to the fourth period is very small. In some cases, the fourth-period element may even have a size comparable to or slightly smaller than the third-period element. This happens due to the poor shielding effect of 3d electrons. The

ineffective shielding allows the nuclear charge to pull the outer electrons closer, reducing the expected increase in size.

- From the fourth to the fifth period, the atomic radius increases significantly. The shielding effect does not change much, but the addition of a new electron shell increases the distance of the valence electrons from the nucleus, leading to a larger atomic size.
- The atomic size again increases, but less than expected. This is because of the poor shielding by 4f electrons present in the elements preceding the sixth-period p-block elements. This phenomenon is related to the lanthanide contraction, which reduces the expected increase in atomic size.

(c) Ionic radius:

Ionic radius is the radius of a monoatomic ion in an ionic crystal structure. Even though ions do not have clear outer boundary, we imagine them as hard spheres. The sizes of these spheres are such that when we add the ionic radius of a cation and an anion, we get the total distance between the two ions in the crystal lattice. The interionic distances in crystals are estimated using X-ray diffraction patterns of ionic crystals. However, there is no obvious way to apportion this distance into cationic and anionic radii. Several indirect methods were proposed to obtain sets of ionic radii consistent with experiments. These radii are also susceptible to change with the actual environment in which an ion occurs.

More recently, detailed electron density contours have been drawn from X-ray data on a number of crystals. The minima in the electron density correspond to the effective boundary of the domain of each ion and, hence, their radii.

Classical Methods for Determining Ionic Radii

Two classical sets of ionic radii were proposed:

(i) **Goldschmidt's Method**:

- Assumed that in crystals formed by large anions with small cations (e.g., LiI), the anions would touch each other. One-half the distance between the anions corresponds to the radius of the anion.
- The interionic distance in crystals of this anion with larger cations (e.g., NaI, KI, etc.) provides the radii of the cations (Na^+, K^+, etc.).
- These values can then be used to determine radii of other anions (e.g., Cl^-).
- The radius of Li^+ can be derived from measurements on LiCl.

Goldschmidt started with the assumption that the molar refractivities of the ions in alkali metal halides (MX) and alkaline earth metal oxides are proportional to their volumes. From measurements on silicate minerals, the radius of the oxide ion (O^{2-}) was estimated to be 132 pm. Goldschmidt compiles a set of ionic radii taking the radius of O^{2-} ion as 132 pm.

(ii) **Pauling's Method**:

Pauling based his calculations on two key assumptions:

(a) For crystals with similar structure (same r_+/r_- ratio), radii of isoelectronic ions vary inversely with their effective nuclear charge:

$$r = \frac{C}{Z_{eff}} = \frac{C}{Z - \sigma}$$

where:

C is a Proportionality constant,

Z is atomic number

and σ is shielding contribution by inner electron core.

(b) He then used experimental interionic distance(d) in crystals of NaF, KCl, RbBr, CsI, and Li_2O (all with $r_+/r_- \approx 0.75$ and adopt NaCl structure).

$$r_+ + r_- = d$$

Pauling's approach may be illustrated taking the example of NaF.

Both Na^+ and F^- have the neon configuration. Shielding contribution, σ for the ions:

[Ne]:$1s^2(2s2p)^8$:

$\sigma = 8 \times 0.35 + 2 \times 0.85 = 4.5$

We can now write radii equations:

$r_{Na^+} = \frac{C}{11-4.5}$; $r_{F^-} = \frac{C}{9-4.5}$

From the observed interionic distance (231 pm), we get

$r_+ + r_- = d$

$\Rightarrow \frac{C}{6.5} + \frac{C}{4.5} = 231$

$\Rightarrow$ C = 614 pm.

Thus:

r_{Na^+}= 95 pm; r_{F^-}= 136 pm.

Pauling calculated the radii of most common ions taking the radius of O^{2-} as 140 pm. Ionic radii estimated by Pauling for univalent ions agree satisfactorily with values obtained by other methods. For multivalent ions, the calculated radii overestimate observed interionic distances.

(iii) **'Crystal' Ionic Radii**

Shannon and Prewitt studied many ionic crystals and measured the distances between cations and anions in those structures. From these distances, they calculated the ionic radii by assuming that the total distance is the sum of the radii of the two ions. They compiled the set of ionic radii based on the radius of O^{2-} as 140 pm. Shannon refined earlier data and provided a set of standard ionic radii for many ions in different oxidation states and coordination numbers. They also considered electronic spin, covalency, repulsive forces, and polyhedral distortion while estimating ionic radii. The ionic radii values compiled by Shannon and Prewitt is known as crystal radii as they conform to actual distances between ions in crystals.

Some General Trends

Ionic radii show same general trends as observed with atomic radii:

(i) *For both cations and anions, the ionic size increases down the group.*

Li^+ (90 pm) < Na^+ (116 pm) < K^+ (152 pm) < Rb^+(166 pm) < Cs^+ (181 pm)

F^- (19 pm) < Cl^- (67 pm) < Br^- (82 pm) < I^- (206 pm)

(ii) *Ionic size decreases from left to right along a period.*

(iii) *The size of a cation is always smaller than that of the atom from which it is formed.*

The appropriate reasons are given below:

- In the formation of a cation, the nuclear charge remains the same but the number of electrons decreases. Thus, the nucleus in a cation attracts the smaller number of electrons towards itself more effectively than it can attract the greater number of electrons of neutral atom.
- In general, all the valence electrons are removed in the formation of a cation, therefore, the number of shells decreases. As a result, size of the cation decreases. Also, the electrons are removed from the relatively larger valence shell orbitals which results in decrease in the size.
- The smaller number of electrons in the cation reduces the electron-electron repulsion, therefore, the electrons shield one another to a lesser extent, and so feel

a stronger pull toward the nucleus. It means that the effective nuclear charge felt by the valence electrons is greater in the cation than in the neutral atom.

(iv) *The size of isoelectronic cations decreases with increase in nuclear charge.*

The isoelectronic species (either atoms or ions) are those which have same number of electrons. Let us consider, for example, three isoelectronic cations in the third period: Na^+, Mg^{2+} and Al^{3+}. The Al^{3+} ion has the same number of electrons as Mg^{2+} but it has one more proton than Mg^{2+}. Thus, the electron cloud in the Al^{3+} ion is pulled inward more effectively than in Mg^{2+} ion. The smaller size of Mg^{2+} ion compared with that of Na^+ can be similarly explained.

(v) *The size of the cations of the same element in different oxidation states decreases with increase in oxidation state.*

For example,

$$Fe^{2+} \text{ (92 pm)} > Fe^{3+} \text{ (78 pm)} > Fe^{4+} \text{ (72 pm)}$$

The nuclear charge in all the three cations is equal (26 protons) but the number of electrons decreases on going from Fe^{2+} to Fe^{3+} to Fe^{4+} ion. Thus, the electron cloud in Fe^{4+} ion is pulled inward more than that in Fe^{3+} ion and the electron cloud in Fe^{3+} ion is pulled inward more than that in Fe^{2+} ion. Since the number of $3d$-electrons decreases on going from Fe^{2+} to Fe^{3+} to Fe^{4+} ion, the electron-electron repulsion decreases in the same direction. Thus, the electrons in $3d$ orbitals in Fe^{2+} ion shield one another more than in Fe^{3+} ion and the $3d$ electrons in Fe^{3+} ion shield one another from nucleus more than in Fe^{4+} ion. Thus, as a result of decrease in shielding effect of electrons, effective nuclear charge increases on going from Fe^{2+} to Fe^{3+} to Fe^{4+}.

The decrease in size of cations with increasing oxidation state is also due to the reason that the increasing cationic charge pulls anion in closer.

(vi) *All monoatomic anions are larger than their parent anion.*

When one or more electrons are added to the neutral atom, an anion is formed. The anionic radius of an element is larger than its atomic radius because the nuclear charge remains the same but the repulsion resulting from the additional electron(s) enlarges the domain of electron cloud and the electrons in the outermost shell orbitals shield more effectively from nucleus than in the neutral atom. As a result, effective nuclear charge decreases.

(vii) *The size of isoelectronic anions decreases with increase in nuclear charge.*

Let us consider, for example, the ionic radii of N^{3-}, O^{2-} and F^{-} ions. All of these ions have 10 electrons in exactly the same orbitals but the nuclear charge (i.e., the number of protons) increases by one unit on going from N^{3-} ion to O^{2-} ion and by one unit on going from O^{2-} ion to F^{-} ion. Thus, force of attraction between nucleus and the electron cloud increases on going from N^{3-} ion to O^{2-} and O^{2-} ion to F^{-} ion. Thus, the size of these ions decreases in the order:

$$N^{3-} > O^{2-} > F^{-}$$

(viii) *For both cations and anions crystal radius increases with increase in co-ordination number.*

For K^{+}, coordination number (CN): 4 (113 pm) < 6 (116 pm) < 8 (132 pm) < 12 (153 pm)

The coordination number refers to the number of oppositely charged ions (counterions) that surround a given ion in a crystal lattice. As the coordination number increases, more ions are arranged around the central ion. This leads to greater repulsive forces among the surrounding counterions due to their close proximity to each other. To reduce these repulsive interactions and achieve a more stable arrangement, the surrounding ions position themselves at slightly greater distances from the central ion. This adjustment leads to an expansion of the ionic environment, effectively increasing the crystal radius of the central ion.

(d) Ionization Enthalpy or Ionization Energy(I)

The ionization energy of an element is the minimum amount of energy required to remove an electron from an isolated gaseous atom in its ground state to produce a cation.

$$A(g) + I \rightarrow A^+(g) + e^-$$

Ionization energy is always positive because removing an electron always takes energy to overcome the attraction of nuclear charge.

For a many-electron atom, the amount of energy required to remove the least tightly bound electron from the neutral atom is called the *first ionization energy* (I_1).

$$A(g) + I_1 \longrightarrow A^+(g) + e^-$$

The energy required to remove the second electron from the unipositive cation is the *second ionization energy* (I_2); the energy required to remove the third electron is the *third ionization energy* (I_3), and so on.

$$A^+(g) + I_2 \longrightarrow A^{2+}(g) + e^-$$

$$A^{2+}(g) + I_3 \longrightarrow A^{3+}(g) + e^-$$

When an electron is removed from the neutral gaseous atom, the cation formed has one fewer electron than the neutral atom, but the number of protons remains the same. As a result, the repulsion among the remaining electrons decreases, and the effective nuclear charge increases. Thus, the cation holds its remaining electrons more tightly. Therefore, the energy required to remove an electron from the cation is greater than that required to remove an electron from the gaseous neutral atom, i.e., $I_2 > I_1$.

Further removal of an electron from the cation results in a dipositive cation. Again, the repulsion among the electrons decreases, and the effective nuclear charge increases. Thus, the dipositive cation holds its electrons even more tightly. As a result, the energy required to remove an electron from the dipositive cation is greater than the energy required to remove an electron from the unipositive cation, i.e., $I_3 > I_2$.

Thus, ionization energies always increase in the following order:

$$I_1 < I_2 < I_3 < \ldots$$

The factors

The factors that influence the ionization energy are:

1. Atomic size,
2. Effective nuclear charge,

3. Shielding or screening effect of the inner shell electrons,
4. Penetration effect of the outer orbitals,
5. Relative stabilities of the electro configurations before and after ionization.

Periodic Trends in Ionization Enthalpy

In a period

For main group (*s* and *p*-block) elements, on going across the period from left to right, the nuclear charge increases from one element to the next by one unit and each additional electron adds to the same outermost shell. The electrons in the same shell do not efficiently shield one another from nuclear charge, therefore, the effective nuclear charge felt by the outermost electrons increases with increase in atomic number in a period. Thus, the force of attraction between the nucleus and the outermost electrons increases with increase in effective nuclear charge. As a result, the outermost electrons are held increasingly tightly to the nucleus. Thus, the first ionization energies of main group elements in a period of the periodic table increase with increase in atomic number.

Some anomalies

The first ionization energies of second period elements increase in the order:

Li < **B < Be** < C < **O < N** < F < Ne

(a) *The first ionization energy of Be is greater than that of B, although B has a greater nuclear charge.*

This can be explained as follows:

Be: $1s^2 2s^2$ B: $1s^2 2s^2 2p^1$

(i) The $2p$ orbital is less penetrating to the nucleus relative to the 2s orbital. So, the $2p^1$ electron in B is better shielded from the nucleus by the inner electrons than the $2s^2$ electrons of Be. Therefore, it is easier to remove the 2p electron from B compared to the 2s electron from Be.

(ii) The 2s orbital in Be is completely filled and is more stable than the $2s^2 2p^1$ configuration. Thus, the energy required to remove an electron from 2p orbital of B is less than that require to remove an electron from 2s orbital of Be.

(b) *The first ionization energy of O is less than that of N.*

This can be explained as follows:

(i) In N ($2s^2 2p^3$), the *p* electrons are in the three separate orbitals. In O ($2s^2 2p^4$), the fourth electron gets paired with one of the three 2p electrons. The proximity of the two electrons in the same orbital results in greater electron-electron repulsion. Thus, it is easier to remove one of the paired electrons in O than one of the unpaired electrons in N.

(ii) The half-filled $2p^3$ orbital of *N* ($2s^22p^3$) is more stable than the $2p^4$ orbital of O.

In a group

Elements in a group have similar outer electronic configuration. In general, in going from top to bottom within a group, the effective nuclear charge as well as the atomic radius increase with increasing number of principal shells. But the effect of increase in atomic size is more significant than the increase in effective nuclear charge. Within a given subshell, orbitals with higher principal quantum numbers are larger than orbitals with smaller principal quantum numbers. Consequently, the electrons in the outermost shell are farther away from the positively charged nucleus. As a result, the force of attraction between the nucleus and the outermost electrons decreases. Therefore, it becomes increasingly easier to remove the first electron on descending a group.

Applications of Ionization Energy

The value of ionization energy helps in explaining many chemical properties of elements. Some important applications are discussed below:

1. Classification of Elements as Metals, Metalloids and Non-metals

Ionization energy helps in determining the metallic and non-metallic character of elements.

- Elements having low ionization energy can lose electrons easily and therefore show metallic (electropositive) character.
- Elements having high ionization energy do not lose electrons easily and tend to gain electrons. Hence, they show non-metallic (electronegative) character.

Periodic trend:

- Across a period (left to right): Ionization energy increases. Therefore, metallic character decreases and non-metallic character increases.
- Down a group: Ionization energy decreases. Hence metallic character increases.

The trend of metallic → metalloid → non-metallic character is particularly noticeable in groups 13–17 of the p-block.

Example (Group 14): C–non-metal, Si, Ge – metalloids, Sn, Pb – metals

2. Reducing Character of Elements

A reducing agent is a substance that loses electrons during a chemical reaction.

- Elements with low ionization energy lose electrons easily and therefore act as strong reducing agents.

Trends:

- Down a group: Ionization energy decreases, so reducing character increases.
- Across a period (left to right): Ionization energy increases, so reducing character decreases, while oxidizing character increases.

For example, the alkali metals show increasing reducing character on going down the group.

In general, metals act as reducing agents, whereas reactive non-metals such as oxygen and halogens act as oxidizing agents.

3. Stability of Oxidation States

Ionization energy also helps to explain the stability of different oxidation states of elements.

- Formation of a higher oxidation state requires the removal of more electrons.
- If the successive ionization energies increase greatly, removal of additional electrons becomes difficult.

Therefore:

- Elements with low ionization energies can easily form higher positive oxidation states.
- When ionization energy increases sharply after removal of a few electrons, higher oxidation states become less stable and lower oxidation states are more stable.

Thus, ionization energy plays an important role in determining the possible and stable oxidation states of elements.

4. Possibility of Formation of Ionic Compounds

Ionization energy also helps in predicting the formation of ionic compounds.

- Elements with low ionization energy lose electrons easily and form positive ions (cations).
- These cations combine with atoms having high tendency to gain electrons to form ionic compounds.

Thus,

- Lower ionization energy → easier loss of electron → greater tendency to form ionic compounds.
- Higher ionization energy → less tendency to form ionic compounds.

(e) Electron Affinity (E_a) or Electron-gain enthalpy ($\Delta_{eg}H°$)

The Electron-gain enthalpy of an element is defined as the standard molar enthalpy change accompanying the addition of an electron to a free gaseous atom of the element in its ground state:

$$A(g) + e^{-}(g) \rightarrow A^{-}(g)$$

Depending on the element, the process of adding electron to the atom can be either endothermic or exothermic. For many elements, energy is released when an electron is added to an isolated gaseous atom and therefore, electron gain enthalpy is negative (electron affinity values in such cases are taken as positive). For example, halogens have very high negative electron-gain enthalpy values. On the other hand, inert gases have positive electron-gain enthalpies (electron affinity values in such cases are taken as negative). When an atom has high tendency to accept electron, large amount of energy will be released and the electron-gain enthalpy will be highly negative (E_a positive).

The Factors

The following are some important factors on which electron-gain enthalpy mostly depends:

(i) *Nuclear charge*

The electron gain enthalpy become more negative as the nuclear charge increases. This is due to greater attraction for the incoming electron if nuclear charge is high.

(ii) *Size of the atom*

With the increase in size of the atom, the distance between the nucleus and the incoming electron increases and this results in lesser attraction. Consequently, the electron gain enthalpy become less negative with increase in size of the atom of the element.

(iii) *Electronic configuration*

The elements having stable electronic configurations of half-filled and completely filled valence subshells show very small tendency to accept additional electron and thus electron gain enthalpies are less negative.

(iv) *The nature of the lowest unfilled atomic orbital*

The magnitude of electron affinity is largely determined by the nature of the lowest unfilled atomic orbital which will accommodate the added electron. An element will normally show a high electron affinity when the added electron enters a shell where it experiences a strong effective nuclear charge and low repulsion from the existing electrons.

Periodic trends

Periodic variations of electron-gain enthalpy are not very regular. However, it has been observed that the electron gain enthalpy, in general, becomes more negative from left to right in a period and becomes less negative as we go from top to bottom in a group. These variations are discussed below:

(a) **Variation down a group.** On moving down a group, the size and nuclear charge increases. But the effect of increase in atomic size is much more pronounced than that of nuclear charge and thus the additional electron feels less attraction by the large atom. Consequently, electron gain enthalpy becomes less negative.

(b) Variation along a period. On moving across a period, the size of the atom decreases and nuclear charge increases. Both these factors result into greater attraction for the incoming electron, therefore, electron gain enthalpy, in general, becomes more negative in a period from left to right.

Important Trends in Electron Gain Enthalpies

There are some important features of electron gain enthalpies of elements. These are:

(i) **Halogens have the highest negative electron gain enthalpies.** The electron gain enthalpies of the halogens (group 17 elements) are highly negative. This is due to the fact that halogens have the general electronic configuration of ns^2np^5 and have only one electron less than the stable noble gas (ns^2np^6) configurations. Thus, they have very strong tendency to accept an additional electron and their electron gain enthalpies are, therefore, highly negative.

(ii) **Electron gain enthalpy values of noble gases are positive.**

The electron gain enthalpy values of noble gases are positive. This is because they have stable electronic configuration of ns^2np^6 and thus they have absolutely no tendency to take an additional electron. This means that the incoming electron enters the next higher principal quantum level and does not feel any attraction for the nucleus. Thus, energy is required to force the electron in their atoms and therefore, their electron gain enthalpies are positive.

(iii) **Electron gain enthalpy of fluorine is unexpectedly less negative than that of chlorine.**

The electron gain enthalpy, in general, becomes less negative from top to bottom in a group. However, it is observed that F-atom has unexpectedly less negative electron gain enthalpy than Cl-atom. The less negative electron gain enthalpy value of F is due to the very small size of F-atom. As a consequence of small size, there are strong interelectronic repulsions in the relatively compact 2p-subshell of fluorine and thus the incoming electron does not feel much attraction. Hence, the element with most negative electron gain enthalpy is chlorine.

(iv) **There is a large decrease in electron-gain enthalpy between Li and Be despite the increase in nuclear charge.**

The electron configurations of Li and Be are $[He]2s^1$ and $[He]2s^2$, respectively. The additional electron enters the 2s orbital of Li but it enters the 2p orbital of Be, and hence is much less tightly bound. In fact, the nuclear charge is so well shielded in Be that electron gain is endothermic.

(v) **The electron-gain enthalpies for some third period elements (e.g. P, S, Cl) are more negative than the corresponding second period members (e.g. N, O, F).**

This is due to the smaller size of the atoms of the second period elements which would produce larger electron-electron repulsions for the additional electron.

(vi) **Nitrogen has negative electron affinity value** ($E_a = -7$ kJmol^{-1} or $\Delta_{eg}H° \approx 0$)

Due to stable half-filled $2p^3$ configuration, nitrogen has little tendency to gain any electron. The incoming electron needs to pair with the already present electron in the same subshell and also face the consequent repulsion.

Problem

Comment on the electron affinity values (kJ mol^{-1}): Na 53; Mg –39.

Solution:

In sodium ($[Ne]3s^1$), the added electron enters the 3s orbital, which gets fully filled. The positive electron affinity value of 53 kJ mol^{-1} implies that the $Na^-(g)$ ion is more stable than the free Na(g) atom by this amount of energy.

In the case of magnesium ($[Ne]3s^2$), the incoming electron must be placed in the 3p orbital, which gets screened by the $3s^2$ core. Hence, the last electron is much less tightly bound, making $Mg^-(g)$ unstable by 39 kJ mol^{-1} with respect to the free atom.

(f) Electronegativity

Concept of electronegativity was introduced by Linus Pauling. Electronegativity is the ability of an atom in a molecule to attract shared electrons in a bond toward itself.

It is evident from this definition that electronegativity is not the property of an isolated atom but rather a property of an atom in a molecule and hence depends on the chemical environment of the atom.

Quantitative measures of electronegativity have been defined in many ways. Some commonly used electronegativity scales are discussed below:

(1) Pauling Electronegativity: Pauling noticed that the bond dissociation enthalpy of a heteronuclear diatomic molecule of the general formula AB is always greater than the average of the bond dissociation enthalpies of the homonuclear molecules A_2 and B_2. Pauling reasoned that the excess bond dissociation enthalpy (Δ) of the A—B bond was due to its ionic character.

The value of Δ was estimated as the difference between the experimental value of bond dissociation enthalpy, $D(A-B)$ and the hypothetical bond dissociation enthalpy. The hypothetical bond dissociation enthalpy was calculated as the average (geometrical mean) of the bond dissociation enthalpies $D(A-A)$ and $D(B-B)$ of the molecules A_2 and B_2:

$$\Delta = D(A-B) - [D(A-A) \cdot D(B-B)]^{1/2}$$

Pauling defined the difference in electronegativity as:

$$[\chi_A - \chi_B]^2 = \Delta$$

or

$$|\chi_A - \chi_B| = \Delta^{1/2}$$

where χ_A and χ_B are the electronegativities of atoms A and B respectively.

If Δ is calculated in $kJmol^{-1}$, the final expression in Pauling’s scale becomes

$$|\chi_A - \chi_B| = 0.102\ \Delta^{1/2}$$

(2) Mulliken Scale: Mulliken defined electronegativity as the arithmetic mean of the first ionization energy and the electron affinity of an atom.

$$\chi_M = \frac{I_1 + E_a}{2}$$

Where I_1 and E_a are the valence state ionization energy (in eV) and electron affinity of the element (in eV), respectively. Values of valence state ionization energy and the valence state electron affinity are calculated from the atom as it exists in a molecule. For example, the valence state of Be is [He]$2s^1 2p^1$ as it always exhibits a valence of two.

The values of electronegativities on Mulliken scale are about 2.8 times as large as those on Pauling scale. Mulliken electronegativity values (χ_M) may be related to Pauling electronegativity (χ_P) through

$$\chi_P = 1.35(\chi_M)^{1/2} - 1.37$$

(3) Mulliken-Jaffe Electronegativities

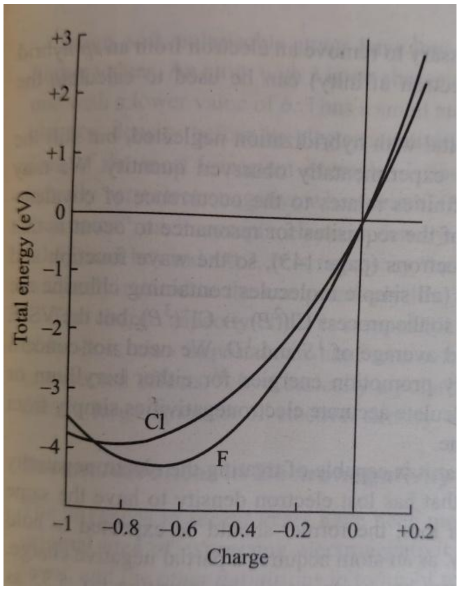
Jaffe electronegativities depend on the charge of the atom. The total energy E (sum of ionization energies or sum of electron affinities) of the ion is related to the ionic charge q by the quadratic equation:

$$E = \alpha q + \beta q^2$$

Jaffe has pointed out that the Mulliken electronegativity is equal to the slope of the energy curve (E vs q) as it passes through the origin. Thus, the Mulliken electronegativity is equal to the derivative of the total energy with respect to charge:

$$\chi_M = \frac{dE}{dq} = \alpha + 2\beta q$$

An atom will be highly electronegative if it releases high energy because its energy curve is steep, and another atom will be less electronegative because its curve is less steep. The energy curve for fluorine is steeper than that of chlorine, indicating that fluorine is more electronegative than chlorine in ClF molecule.



(4) Allred and Rochow Electronegativity

Allred and Rochow (in 1958) defined electronegativity as the electrostatic force of attraction existing between the nucleus and the valence electrons in an atom. This electrostatic force of attraction, F is given by Coulomb's Law:

$$F = \frac{Z_{eff}\, e^2}{r_{cov}}$$

Where Z_{eff} is the effective nuclear charge at the periphery of the atom, e is the charge on the electron and r_{cov} is the covalent radius of the atom. The forces obtained in this way can be adjusted to the Pauling scale by plotting them against Pauling's values (Plot is not given here). A plot of Pauling electronegativities against F gives an approximately a straight line. From the slope and intercept of the straight line, the Allred-Rochow electronegativities (on Pauling scale) are obtained by the relationship:

$$\chi_{AR} = \frac{0.3590\, Z_{eff}}{(r_{cov}|pm)^2}$$

According to Allred-Rochow, elements with high electronegativities are those with high effective nuclear charge and small covalent radii.

Factors Affecting the Magnitude of Electronegativity

Several factors that influence the magnitude of electronegativity are as follows:

(1) Size of the Atom: In general, smaller atoms have a greater attraction for shared electron pair than larger ones. Hence the smaller atoms are more electronegative than larger ones. For example, fluorine is smaller in size than oxygen, therefore, fluorine has greater electronegativity (4.0) than oxygen (3.5).

(2) Effective Nuclear Charge: Higher the effective nuclear charge, Z_{eff} of an element, greater will be the attraction to the shared pair of electrons and hence a higher electronegativity.

(3) Electronic Configuration: An element which attains a stable configuration of the next noble gas by gaining few electrons will be more electronegative than one which requires many. For example, F($1s^2 2s^2 2p^5$) is more electronegative than O($1s^2 2s^2 2p^4$) which in turn is more electronegative than N($1s^2 2s^2 2p^3$) because F requires 1, O requires 2 and N requires 3 electrons to attain the configuration of Ne.

(4) Ionization Energy and Electron Affinity: According to Mulliken, the electronegativity is the average of ionization energy and electron affinity of an atom. Thus, an atom such as F which has a high ionization energy and a high electron affinity, has a high electronegativity.

(5) Electropositive Character: Electropositive character of an element is opposite of its electronegative character, i.e., the elements which are highly electropositive, are less electronegative. The electropositive character is also related to the ionization energy and the electron affinity. The elements having lower values of ionization energy and electron affinity are more electropositive and hence are less electronegative.

(6) Oxidation State of the Element: If an atom has high partial positive charge or high positive oxidation state, then it has a high tendency to attract a shared electron pair and hence high electronegativity. By contrast, an atom having a high partial negative charge or high negative oxidation state, has larger size and low Z_{eff}. Thus, an anion has less tendency to attract shared electron pair and hence less electronegativity than its parent atom.

If an element shows variable positive oxidation states, its size decreases and effective nuclear charge increases with increase in its positive oxidation state. For example, the size of Fe decreases in the order: $Fe > Fe^{2+} > Fe^{3+}$ and effective nuclear charge increases in the order: $Fe < Fe^{2+} < Fe^{3+}$. Thus, the electronegativity increases in the order:

$$\chi_{Fe} < \chi_{Fe^{2+}} < \chi_{Fe^{3+}}$$

In the similar way, the variation in electronegativity of Cl atom can be seen in its oxo-acids, HClO, $HClO_2$, $HClO_3$ and $HClO_4$. Oxidation states of Cl atom in HClO, $HClO_2$, $HClO_3$ and $HClO_4$ are +1, +3, +5 and +7 respectively. Thus, electronegativity of Cl atom in its oxo-acids increases in the order:

$$HClO < HClO_2 < HClO_3 < HClO_4$$

Since an anion has larger size and lower effective nuclear charge than its parent atom, the anion has less ability to attract shared electron pair toward itself and hence has a lower value of electronegativity.

(7) Type of Hybridization: We know that s electrons are more penetrating than the p electrons. Thus, an atom having hybrid orbitals with a greater s-character in a molecule, has electron density closer to the nucleus of that atom and experience greater effective nuclear charge. So, as the *s*-character increases, the ability of the atom to attract shared pair of electrons increases. Hence the electronegativity of the atom increases with increase in *s*-character in the hybrid orbital. In CH_4, C_2H_4 and C_2H_2, for example, C atom is sp^3, sp^2 and *sp* hybridized respectively. Hybrid orbitals in CH_4 (sp^3-hybridization), C_2H_4 (sp^2-hybridization) and C_2H_2(*sp*-hybridization) have 25%, 33.33% and 50% *s*-character respectively. Thus, the ability of C-atom to attract shared electron pairs and hence electronegativity increases in the order:

$$CH_4 < C_2H_4 < C_2H_2$$

Therefore, acidic character of the hydrocarbons increases in the same order.

(8) Effect of Substituents: Electronegativity of an atom in molecules also depends on the nature of the substituents or groups attached to that atom. Let us discuss, for example, the variation of electronegativity of C-atom in CH_3I and CF_3I molecules. Since F atom in CF_3I molecule is most electronegative, it attracts shared electron pair of C—F bond strongly. Thus, carbon atom in CF_3I molecule bears a positive charge and it becomes more electronegative than I. Now the positively charged C polarizes the C—I bond strongly. As a result, the entity CF_3 bears a partial negative charge and I bears a partial positive charge: $CF_3^{\delta-}I^{\delta+}$. In CH_3I molecule, C is less electronegative than I, so $CH_3^{\delta+}I^{\delta-}$. This discussion shows that C is more electronegative in CF_3I than in CH_3I. Different electronegativities of C atom in these molecules explain why different products are obtained when CH_3I and CF_3I are hydrolyzed.

$$CH_3I + HOH \longrightarrow CH_3OH + HI$$

$$CF_3I + HOH \longrightarrow IOH + HCF_3$$

(9) Bond Order: As the bond order between two atoms of a diatomic molecule increases, bond length decreases because the size of the atoms decreases. As a result, electronegativity of the atom increases. For example, electronegativity of carbon in C—C bond is less than that in C=C bond and electronegativity of C in C=C bond is less than that in C≡C bond.

Variation of Electronegativity of Main Group Elements

(1) In a Period: On going left to right across a period, the electronegativity of elements increases because:

(i) size of atoms decreases,

(ii) effective nuclear charge increases.

For example, electronegativity of third period elements increases in the order:

$$Li(1.0) < Be(1.5) < B(2.0) < C(2.5) < N(3.0) < O(3.5) < F(4.0)$$

(2) In a Group: On going top to bottom within a group electronegativity decreases because size of atoms increases,

For example, electronegativity of halogens decreases on descending the group:

$$F\ (4.0) > Cl\ (3.1) > Br\ (2.9) > I\ (2.6)$$

Note that fluorine is most electronegative and francium is least electronegative in the periodic table.

Applications of Electronegativity

(1) To Predict the Nature of Bond: Atoms of elements with widely different electronegativities (electronegativity difference ≥ 1.7) tend to form ionic compounds such as NaCl and CaO because the atoms of less electronegativity (mostly metals, i.e., electropositive elements) give up their valence electron(s) to the other atom of the more electronegative element (mostly non-metals). Atoms of elements with electronegativity difference ≤ 1.7 tend to form polar covalent bonds with each other because of the shift of electron density toward the more electronegative element (examples HF, HCl, HBr, HI, H_2O, H_2S, NH_3, etc.). Atoms of an element or atoms of different elements with similar electronegativities (usually non-metals) tend to form non-polar covalent bond with each other because there is no significant shift of shared electron pair toward any atom. For example, bonds in H_2, N_2, O_2 and F_2 are non-polar covalent bonds.

Sanderson's Electron Density Ratio

Sanderson considered electronegativity to be a function of compactness of the atom. The electron density ratio or the stability ratio or electronegativity *S*, is defined as:

$$S = \frac{D_i}{D}$$

where *D* is the electron density on the atom

$$D = \frac{3Z}{4\pi r^3}$$

and D_i is the ideal electron density of the hypothetical isoelectronic inert gas atom. The term D_i is determined by linear extrapolation between *D* values for the next higher and the next lower inert gases. These *S* values are adjusted to Pauling scale by the relationship:

$$\chi^{1/2} = 0.21S + 0.77$$